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L3: Entry 1 of 1 File: DWPI Aug 28, 2001

DERWENT-ACC-NO: 1999-573912
DERWENT-WEEK: 200151

TITLE: Multilayer interference pigments for use in polymers, lacquers, inks, cosmetics, glass, security documents or paper

< u>Patent Serial Number (1):
6280520

Basic Abstract Text (1):
NOVELTY - Multilayered nacreous pigments with a nonmetallic, platelet-form opaque or semi-opaque substrate comprise (a) a first layer of a metal oxide with a high RI or of a metal; (b) a second layer of a low RI metal oxide; (c) a third layer as per (a); and optionally also (d) a top layer.

Basic Abstract Text (5):
USE - Claimed uses are in pigmenting lacquers, printing inks, plastics, cosmetics, glasses for ceramics, or glass, preferably in admixture with conventional and other effect pigments; in pigmenting of security documents or packages; or in laser marking of polymeric materials or paper.

Equivalent Abstract Text (1):
NOVELTY - Multilayered nacreous pigments with a nonmetallic, platelet-form opaque or semi-opaque substrate comprise (a) a first layer of a metal oxide with a high RI or of a metal; (b) a second layer of a low RI metal oxide; (c) a third layer as per (a); and optionally also (d) a top layer.

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Search Results - Record(s) 1 through 2 of 2 returned.

☐ 1. Document ID: US 20020077380 A1

L2: Entry 1 of 2 File: PGPB Jun 20, 2002

PGPUB-DOCUMENT-NUMBER: 20020077380
PGPUB-FILING-TYPE: new
DOCUMENT-IDENTIFIER: US 20020077380 A1

TITLE: Laser-writable polymer composition

PUBLICATION-DATE: June 20, 2002

INVENTOR-INFORMATION:

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Wessels, Esther	Emmen		NL	
Higler, Johannes F.	Elsloo		NL	

US-CL-CURRENT: 522/2; 524/409

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw Desc | Image

☐ 2. Document ID: US 6280520 B1 EP 950693 A1 DE 19817286 A1 CN 1232843 A JP 2000001628 A KR 99083277 A MX 9903590 A1

L2: Entry 2 of 2 File: DWPI Aug 28, 2001

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TITLE: Multilayer interference pigments for use in polymers, lacquers, inks, cosmetics, glass, security documents or paper

INVENTOR: ANDES, S; BRUECKNER, D ; FUCHS-POHL, G ; KUNTZ, M ; PFAFF, G ; VOGT, R ; BRUCKNER, D

PRIORITY-DATA: 1998DE-1017286 (April 18, 1998)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
US 6280520 B1	August 28, 2001		000	C04B001/32
EP 950693 A1	October 20, 1999	G	013	C09C001/00
DE 19817286 A1	October 21, 1999		000	C09B001/00
CN 1232843 A	October 27, 1999		000	C09C003/06
JP 2000001628 A	January 7, 2000		010	C09C003/06
KR 99083277 A	November 25, 1999		000	C09C001/28
MX 9903590 A1	August 1, 2000		000	C09C001/24

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L2: Entry 2 of 2 File: DWPI Aug 28, 2001

DERWENT-ACC-NO: 1999-573912
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provided by an interpolymerized C_4–C_{10} vinylene monobasic carboxylic acid monomer. Moreover, disclosed in U.S. Pat. No. 4,481,244 is a material that can be selected for writing or printing, which comprises a substrate and coating layer formed thereon of a coating material containing a polymer having both hydrophilic segments and hydrophobic segments.

Additionally, there is disclosed in U.S. Pat. No. 3,790,435 and U.S. Pat. No. 4,318,950 synthetic papers and methods for the preparation thereof. The term synthetic paper as indicated on page 1, line 20, of U.S. Pat. No. 4,318,950 refers to a paper like laminar structure in the form of thin sheets or films of synthetic resinous material employed for various uses such as writing or printing, as distinguished from natural cellulose paper. Synthetic papers comprised of thermoplastic resins or papers coated with polymeric emulsions are known for use in writing and printing. Disclosed in U.S. Pat. No. 3,380,868 are oriented thermoplastic film laminated structures which can be selected for various imaging processes. Polymeric film structures having a matte-finish and a cellular structure achieved with the addition of fillers which roughens the surface upon stretching of the films and renders them receptive to marking by crayons, pencil and ball-point pen are disclosed in U.S. Pat. No. 3,154,461. Laminates comprising layers of oriented films of thermoplastic materials in which at least one of the outermost layers contains a suitable inert additive are disclosed in U.S. Pat. No. 3,515,626. These laminates are useful in films which may be written on by a pencil or a crayon.

Disclosed in U.S. Pat. No. 3,790,435 are synthetic papers with acceptable foldability of a nonlaminated structure of one thermoplastic resin film or a laminated structure of at least two thermoplastic resin films, see the Abstract of the Disclosure for example. Each of the films is stretched or molecularly oriented, and one or more of the films contain a fine inorganic filler to provide paperness of the film. According to this patent some of the films may contain certain amounts of poly(styrene) as a foldability improving agent.

There is disclosed in U.S. Pat. No. 4,663,216 a synthetic paper printable in high gloss, and comprised of (1) a multilayer support, (2) a layer of a transparent film of a thermoplastic resin free from an inorganic fine powder formed on one surface of the support (1), and (3) a primer layer of a specific material, reference the Abstract of the Disclosure for example. The support (1) comprises (1a) a base layer of a biaxially stretched film of a thermoplastic resin, a surface and a back layer (1b), and (1c) composed of a monoaxially stretched film of a thermoplastic resin containing from 8 to 65 percent by weight of an inorganic fine powder.

Further, there is disclosed in U.S. Pat. No. 4,705,719 a synthetic paper of multilayer resin films comprising a base layer (1a) of a biaxially stretched thermoplastic resin film, and a laminate provided on at least one of opposite surfaces of said base layer, the laminate including a paper-line layer (1b) and a surface layer (1c), the paper-like layer containing a uniaxially stretched film of a thermoplastic resin containing 8 to 65 percent by weight of inorganic fine powder, said surface layer being constituted by a uniaxially stretched film made of a thermoplastic resin. Also known is an electrostatic recording material comprised of a multi-layered sheet support having an electroconductive layer and dielectric layers formed successively thereon, reference for example U.S. Pat. No. 4,795,676.

Never-tear plastic papers (3R109 durable paper available from Xerox Corporation) comprised of a polyester base containing a coating blend of certain binders with titanium dioxide are also known. These aforementioned papers are useful in a single sided xerographic imaging process, however, they possess disadvantages when selected for duplex imaging systems in that, for example, there is an electrostatic buildup of charges during the first printing cycle on one side thereby preventing the paper from a consistent automatic feeding through the xerographic imaging device a second time. Another type of never-tear plastic paper is comprised of an opaque polyester base containing a binder, an antistatic agent and titanium dioxide. These papers possess acceptable charging and discharging characteristics for duplex printing but have disadvantage that the toner in the imaged areas does not fix well to the paper. The disadvantages of these two types of never-tear papers are overcome with the never-tear papers of the present invention wherein the receiving layer is free of pigment such as titanium dioxide as well as an antistatic agent thereby resulting in excellent toner fix primarily because of the presence of, for example, hydroxypropyl cellulose in the pigmented layer underneath the toner receiving layer. The pigmented layer also acts as an antistatic layer, in some embodiments and ensures proper charging and discharging behavior, and thus there is no electrostatic buildup on these never-tear papers resulting in their being ideal for duplex printing.

Also a number of transparencies with, for example, coatings are known, reference for example U.S. Pat. Nos. (1) 3,535,112, which illustrates transparencies with polyamide overcoatings; (2) 3,539,340 wherein transparencies with vinyl chloride overcoatings are described; (3) 4,072,362 which discloses transparencies with overcoating of styrene acrylate or methacrylate ester polymers; (4) 4,085,245 wherein there is disclosed transparencies with blends of acrylic polymers and vinyl acetate polymers; (5) 4,259,422 which discloses, for example, transparencies with hydrophilic colloids; (6) 4,489,122 wherein there is disclosed transparencies containing elastomeric polymers overcoated with poly(vinylacetate), or terpolymers of methylmethacrylate, ethyl acrylate, and isobutylacrylate; and (7) 4,526,847 which discloses transparencies containing coatings of nitrocellulose and a plasticizer.

There are described in the U.S. Pat. No. 4,956,225 transparencies suitable for electrographic and xerographic imaging comprised of a polymeric substrate with a toner receptive coating on one surface thereof, which coating is comprised of blends of poly(ethylene oxide) and carboxymethyl cellulose; poly(ethylene oxide), carboxymethyl cellulose and hydroxypropyl cellulose; poly(ethylene oxide) and vinylidene fluoride/hexafluoropropylene copolymer, poly(chloroprene) and poly(α-methylstyrene); poly(caprolactone) and poly(α-methylstyrene); poly(vinylisobutylether) and poly(α-methylstyrene); blends of poly(caprolactone) and poly(p-isopropyl α-methylstyrene); blends of poly(1,4-butylene adipate) and poly(α-methylstyrene); chlorinated poly(propylene) and poly(α-methylstyrene); chlorinated poly(ethylene) and poly(α-methylstyrene); and chlorinated rubber and poly(α-methylstyrene). Further, in another aspect of the U.S. Pat. No. 4,956,225 there are provided transparencies suitable for electrographic and xerographic imaging processes comprised of a supporting polymeric substrate with a toner receptive coating on one surface thereof comprised of: (a) a

first layer coating of a crystalline polymer selected from the group consisting of poly(chloroprene), chlorinated rubbers, blends of poly(ethylene oxide), and vinylidene fluoride/hexafluoropropylene copolymers, chlorinated poly(propylene), chlorinated poly(ethylene), poly(-vinylmethyl ketone), poly(caprolactone), poly(1,4-butylene adipate), poly(vinylmethyl ether), and poly(vinyl isobutylether); and (b) a second overcoating layer comprised of a cellulose ether selected from the group consisting of hydroxypropyl methyl cellulose, hydroxypropyl cellulose, and ethyl cellulose.

Additionally there is described in the copending application, U.S. Pat. No. 4,997,697 entitled "Transparencies" with the listed inventor Shadi Malhotra, a transparency comprised of a supporting substrate, an antistatic polymer layer coated on one or both sides of the substrate comprised of hydrophilic cellulosic derivatives, and toner receiving polymer layer thereover on both sides of the antistatic layer comprised of hydrophobic cellulose ethers and cellulose esters in combination with low melt adhesives. Other transparency coatings include blends of poly(ethylene oxide) with carboxymethyl cellulose as illustrated in U.S. Pat. No. 4,592,954, the disclosure of which is totally incorporated herein by reference, blends of carboxymethyl cellulose, poly(ethylene oxide) and hydroxypropyl cellulose, reference U.S. Pat. No. 4,865,914 blends of hydrophilic cellulosic and plasticizers, reference U.S. Pat. No. 5,006,407, the disclosure of which is totally incorporated herein by reference. Further, disclosed in the patent is a transparency comprised of a supporting substrate on an oil absorbing polymer layer on both sides of the substrate and an ink receiving polymer layer thereon. The ink receiving layer may contain fillers.

Although the papers illustrated in the prior art are suitable for their intended purposes, there remains a need for papers with new coatings thereover that are useful in ink jet printing processes, electrophotographic imaging and printing processes, including color processes, and that will enable the formulation of images with high optical densities. Additionally, there is a need for never-tear papers that can be selected for duplex copying processes. Another need of the present invention resides in providing papers with coatings that do not block (stick) at, for example, 50 percent relative humidity and at a temperature of 50° C. Further, there is a need for never-tear papers that avoid or minimize jamming at the fuser roll, thus shorting the life thereof. Also, there is a need for static-free never-tear papers, or wherein the static charge thereon is minimized or substantially avoided. Another need resides in the provision of never-tear papers for ink jet, dot matrix, typewriters and crayon printing processes, and wherein images of high optical density, such as greater than one, are obtained in embodiments of the present invention.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide papers with many of the advantages illustrated herein.

Another object of the present invention resides in the provision of ink jet papers, or xerographic papers with certain coatings thereover.

Also, in another object of the present invention there are provided papers with certain coatings thereover thus enabling images with high optical densities.

Another object of the present invention resides in ink jet never-tear papers that permit the substantial elimination of beading caused by poor inter-drop coalescence during mixing of the primary colors to generate secondary colors such as, for example, mixtures of cyan and yellow enabling green colors.

Furthermore, in another object of the present invention there are provided electrophotographic never-tear papers that enable elimination of bleeding of colors due to intermingling or diffusion of the dry toners when different colors, for example black, are printed together with another color like magenta.

Additionally, another object of the present invention relates to never-tear papers with a number of top coatings thereover containing colloidal silica enabling such coatings to be particularly useful in printing processes such as dot matrix printers, typewriters and with pencil crayons.

Another object of the present invention relates to ink jet papers with specific coatings which enable, for example, water and glycol absorption from the inks selected in a rapid manner thereby permitting such papers to be particularly useful in known ink jet printers.

In yet another object of the present invention there are provided coatings which are compatible with filled papers, sized papers and opaque Mylars, which coatings will enable the aforementioned materials to generate high optical density images with electrophotographic processes utilizing, for example, liquid toners comprised of a toner resin dispersed in a solvent such as Isopars.

Additionally, in another object of the present invention there are provided low dielectric never-tear papers wherein the ink receiving layer is free of titanium dioxide and an antistatic agent thereby resulting in, for example, excellent toner fix during electrographic and electrophotographic processes.

These and other objects of the present invention are accomplished by providing papers with coatings thereover. More specifically, in accordance with one embodiment of the present invention there are provided papers with coatings thereover which are compatible with the inks, or dry toners selected for marking, and wherein the coatings enable acceptable optical density images to be obtained, especially in duplex imaging processes. In one embodiment of the present invention there are provided never-tear papers comprised of a supporting substrate preferably coated on both sides with a polymer binder resin containing a pigment (pigmented layer), and an ink receiving, layer in contact with both sides of the aforementioned pigmented layers, which ink receiving layer is comprised of, for example, a blend of chlorinated rubber with ethylene/vinyl acetate.

Embodiments of the present invention include a paper comprised of a plastic supporting substrate, a binder layer comprised of polymers selected from the group consisting of (1) hydroxypropyl cellulose, (2) poly(vinyl alkyl ether), (3) vinyl pyrrolidone/vinyl acetate, (4) quaternized vinyl pyrrolidone/dialkylaminoethyl/methacrylate, (5) poly(vinyl pyrrolidone), (6) poly(ethylene imine), and mixtures thereof, and a pigment, or pigments; and an ink receiving polymer layer; and more specifically a coated never-tear paper comprised of a plastic supporting substrate, a resin binder layer in contact with the substrate and comprised of polymers selected from the group consisting of (1) hydroxypropyl cellulose, (2) poly(vinyl alkyl ether), (3) vinyl pyrrolidone/vinyl acetate, (4) quaternized vinyl pyrrolidone/dialkylaminoethyl/methacrylate, (5) poly(vinyl pyrrolidone), (6) poly(ethylene imine), and mixtures thereof, and an inorganic pigment or

ing of 25 μm in thickness of hydroxypropyl cellulose with 20 percent by weight of titanium dioxide coated on a polyester accepted a charge of about 1,150 volts, retained charge in the dark and decayed with exposure to light. With incorporation of 10 percent by weight of poly(N,N-dimethyl-3,5-dimethylene piperidinium chloride) to the aforementioned coating blend of hydroxypropyl cellulose and titanium dioxide, and coating thereof on the polyester, a coated paper was obtained which accepted a charge of 750 volts and decayed instantly when exposed to light. Replacing poly(N,N-dimethyl-3,5-dimethylene piperidinium chloride) with poly(dimethylamineco-epichlorohydrin) quaternized in the aforementioned pigmented coating of hydroxypropyl cellulose with titanium dioxide on polyester, the maximum charge acceptance dropped to 250 volts. Increasing the amount of poly(dimethylamine-epichlorohydrin) quaternized to 40 percent by weight in the pigmented coating of hydroxypropyl cellulose and titanium dioxide, the maximum charge acceptance dropped to 50 volts. At a 40 percent by weight level of poly(N,N-dimethyl-3,5-dimethylene piperidinium chloride) in the pigmented coating of hydroxypropyl cellulose and titanium dioxide, the maximum charge acceptance was 60 volts. These results evidence that the maximum charge acceptable level in never-tear papers of the present invention can be controlled by the amount of the antistatic agent added to the pigmented coating. The preferred value of maximum charge acceptance for papers used in Xerox machines, such as Xerox 1005 TM, is between 125 to 300 volts. The copy quality of images on never-tear papers of the present invention did not show substantial differences between high charge (1,150 volts) acceptance papers or low charge (60 volts) papers. Moreover, the coated never-tear papers of the present invention with high or low charge acceptance did not pose any problem during duplexing providing no residual charge remained after the first cycle. The preferred poly(electrolyte) antistatic agents that can be used in effective amounts of about 10 to about 40 percent by weight in combination with hydroxypropyl cellulose, or other resin binders, and inorganic pigments, such as white titanium dioxide, are poly(dimethylamine-epichlorohydrin) quaternized and poly(N,N-dimethyl3,5-dimethylene piperidinium chloride) due to their high poly(electrolyte) strength, and as these are good cobinders for titanium dioxide. All these poiy(electrolytes) are available commercially, Scientific Polymer Products being one of these sources.

The white or colored pigmented layer can contain pigment components in various effective amounts, such as for example for about 2 to about 50 percent by weight of the pigment binder. Examples of pigments that may be used include titanium dioxide present, for example, in one embodiment in an amount of 20 weight percent (available as Rutile or Anatase from NL Chem Canada Inc.); hydrated alumina (Hydrad TMC, Hydrad TM HBF, Hydrad TM HBC, J. M. Huber Corporation), barium sulfate (K.C. Blanc Fix HD80, available from KaliChemie Corporation) (Opalex-C); blend of calcium fluoride and silica (Opalex-C, Kemira OY); calcium carbonate (Microwhite 0.7/paper, Sylacauga Calcium Products, Kaowhite, available from Thiele Kaolin Company, Pfinyl 402 Pfizer Pigments and Metal Division); high brightness clays (ultra gloss 90[x] Engelhard paper clays, Astra-paque and Altowhite TE Georgia Kaolin); Dow plastic pigments (722, 788 available from Dow Chemicals), zinc oxide (Zoco Fax 183, ZoChem); and blend of zinc sulfide with barium sulfate (Lithopane, available from Sachteben Company). While it is not desired to be limited by the theory, it is believed that the primary purpose of the pigment is to pacify the substrate.

Specific examples of binders include hydroxypropyl cellulose in methanol (75 percent by weight) and a water (25 percent by weight) mixture (available from Klucel, Type E, Hercules), poly(ethylene imine) in water (Scientific Polymer Products), poly(vinyl methyl ether) in water (Gantrez M-154, GAF Corporation), poly(vinyl pyrrolidone) (PVPK-60 GAF Corporation) in methanol, vinyl pyrrolidone/vinyl acetate copolymer in isopropanol, 75 percent by weight, and water, 25 percent by weight, (vinyl acetate content, 50 percent by weight, Scientific Polymer Products), vinyl pyrrolidone/dimethyl amino ethylmethacrylate quaternized in water (#372, Scientific Polymer Products), with hydroxypropyl cellulose being preferred primarily because of its availability, excellent binding characteristics, and effective antistatic properties.

Illustrative examples of substrates with a thickness of, for example, from about 50 microns to about 150 microns, and preferably of a thickness of from about 50 microns to about 75 microns that may be selected for the coated papers include Mylar, commercially available from E.I. DuPont; Melinex, commercially available from Imperials Chemical, Inc.; Celanar, commercially available from Celanese; polycarbonates, especially Lexan; polysulfones; cellulose triacetate; polyvinylchlorides, cellophane; and the like, with Mylar being particularly preferred in view of its availability and lower costs.

Illustrative examples of ink receiving layers of, for example, a thickness of from about 2 to about 25 microns, preferably for each side of the pigmented layer and in contact with the pigmented layer comprised of polymer resin bider and pigment, preferably an inorganic pigment such as titanium dioxide dispersed therein, include poly(ethylene succinate) (available from Scientific Polymer Products) in dichloromethane, poly(diallyl phthalate) (Scientific Polymer Products) in acetone, poly(diallylisophthalate) (Scientific Polymer Products) in acetone, cellulose propionate in acetone (Scientific Polymer Products), ethylene-vinyl acetatevinyl alcohol terpolymer (with ethylene contents of 40 percent by weight, vinyl acetate content of 40 percent by weight, and vinyl alcohol content of 20 percent by weight in acetone) which can be obtained by partial hydrolysis of ethylene vinyl acetate copolymer with vinyl acetate content of 60 percent by weight (available from Scientific Polymer Products); blends of chlorinated rubber (chlorine content 65 percent by weight, available from Scientific Polymer Products) from about 10 to about 90 percent by weight and ethylene/vinyl acetate copolymer (vinyl acetate content 40 percent by weight) from about 90 to about 10 percent by weight in dichloromethane as well as in toluene; blends of chlorinated rubber (chlorine content 65 percent by weight, Scientific Polymer Products) from about 10 to about 90 percent by weight and poly(caprolactone) (PLC-700, available from Union Carbide) from about 90 to about 10 percent by weight in dichloromethane; blends of chlorinated rubber (chlorine content 65 percent by weight, Scientific Polymer Products) from about 10 to about 90 percent by weight and poly(chloroprene) (Scientific Polymer Products) from about 90 to about 10 percent by weight in dichlormethane; blends of poly(-